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ABSTRACT

In this work phase diagrams were constructed for the Cr-Fe-Mo and Cr-Fe-W ternary systems containing up to 55% of iron and up to 30% of molybdenum or tungsten. Hardness and resistance to air oxidation at elevated temperatures were also determined for some of the alloys.

One may assume that under favorable circumstances it is possible /108\*  
to obtain <sup>an</sup> alloy which would combine the most valuable properties of its components: heat resistance of molybdenum or tungsten, thermal stability of chromium and working properties (plasticity) of iron. In the organization of this research it was assumed that the addition of molybdenum or tungsten to iron-chromium alloys will increase their heat resistance without changing significantly their plasticity and thermal stability. Therefore, one of the most important problems of this investigation was to determine the region

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\*Numbers given in margin indicate pagination in original foreign text.

of  $\alpha$ -solid ~~solid~~ solution in the ternary systems up to the solidus temperature and to study the possibility of supercooling it down to room temperature without the formation of  $\sigma$ -phase.

The phase diagrams of Fe-Cr, Fe-Mo, Fe-W, Cr-Mo and Cr-W binary systems have been investigated in great detail (ref. 1, 2). In the Fe-Cr system a continuous solubility was established between  $\alpha$ -iron and chromium. Below  $900^{\circ}$  C the  $\sigma$ -phase is formed as a result of ordering of the solid solution. The infinite solubility of components is also observed in Cr-Mo and Cr-W systems. In the Cr-W system below  $1500^{\circ}$  C decomposition of the solid solution into two solid solutions of different concentrations is observed. In the Fe-Mo system two intermetallic compounds are formed:  $\epsilon$ -Fe<sub>7</sub>Mo<sub>6</sub> and  $\sigma$ , and in the Fe-W system the formed compounds are Fe<sub>2</sub>W and  $\xi$ -Fe<sub>7</sub>W<sub>6</sub>. /109

In reference 4 certain properties of the Fe-Cr-Mo and Fe-Cr-W alloys were investigated (hardness at elevated temperatures, heat resistance, thermal stability, elastic modulus, thermal expansion coefficient, density and plasticity).

The isothermal cross section for the ternary phase diagram of the Fe-Cr-Mo system at 1300, 1100 and  $900^{\circ}$  C were constructed in reference 5. The  $\sigma$ -phase region is extended over a broad concentration region when the amount of molybdenum is increased. This region is adjacent to the  $\sigma$ -phase of the Fe-Mo system. In the above reference it was shown that 120 hr annealing is definitely too short to achieve phase equilibrium in ternary alloys.

The power metallurgical study of the phase composition of the ternary Fe-Cr-Mo alloys, annealed for ten days at  $650^{\circ}$  C enabled the authors of reference 6 to construct the isothermal section of the diagram at this temperature.

The only work which is related to the phase diagram of the Cr-Fe-W system <sup>Cr-Fe-Mo and</sup> is the work of Goldschmidt (ref. 3). He investigated cermets of the  $\Delta$ Cr-Fe-W systems after 60 hour annealing at 620° C. It was shown that in the Cr-Fe-W system the addition of tungsten expands the  $\sigma$ -phase region, and the single phase region of the  $\xi$ -phase ( $\text{Fe}_7\text{W}_6$ ) extends all the way to 60 atom % of chromium. In the Cr-Fe-Mo system the addition of Mo also expands the  $\sigma$ -phase region. In addition to  $\sigma$ -phase Goldschmidt discovered in this system a ternary compound N (apparently  $\text{Fe}_4\text{CrMo}_2$ ).

The authors of reference 7 who investigated the Cr-Fe-Mo alloys, constructed isothermal cross sections of this ternary system at 815 and 900° C. They found a ternary chemical compound, which they called  $\chi$ -phase (approximately  $\text{Fe}_3\text{CrMo}$ ) which has a complex cubic lattice of the  $\alpha$ -Mn type. This phase is not identical with <sup>the</sup>  $\Delta$ N-phase, discovered by Goldschmidt (ref. 3).

In reference 8 the boundary was defined between  $\alpha$  and  $\alpha + \sigma$ -phase /110 regions of the Fe-Cr-Mo ternary system at 1000° C. Figure 1, taken from this reference, clearly shows the space position of the  $\sigma$ -phase in the ternary system.

The work of the Japanese authors (ref. 9) is the most extensive investigation of the Cr-Fe-Mo alloys. It verifies the formation of the ternary compound- $\chi$ -phase, but the formation of N-phase has not been detected. A number of polythermal and isothermal cross sections of the diagram are presented for a series of alloys as well as <sup>for</sup>  $\Delta$ solidus and liquidus temperatures.

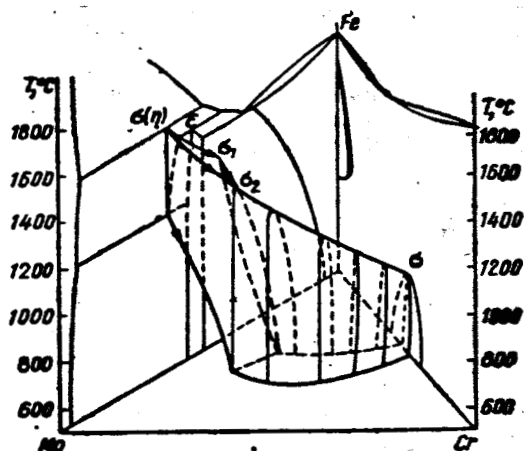


Figure 1. The single phase region of the  $\sigma$ -phase in the Cr-Fe-Mo system (ref. 8).

#### MATERIALS AND METHOD

The following materials were used for the production of alloys:

- 1) electrolytically refined chromium, 99.9 percent pure; the major impurities were: Fe-0.04 percent; Ni-0.002 percent; Si-0.001 percent; N-0.008-0.015 percent; C-0.003-0.007 percent; O-0.001-0.005 percent;  $H_2$ - $10^{-5}$ K percent;
- 2) carbonyl iron in <sup>powder</sup> ~~powder~~ form containing: Si-0.00025 percent, Mg-0.0001 percent; Cu-0.00005 percent; Ni-0.0008 percent; C-0.02 percent; it was remelted in  $10^{-4}$ - $10^{-5}$  mm vacuum and was not analyzed after remelting;
- 3) molybdenum in — bars — 99.9 percent pure; the main impurities were:  $R_2O_3$ -0.01 percent, Ni-0.001 percent,  $SiO_2$ -0.001 percent, CaO + MgO - traces;
- 4) tungsten in — bars — 99.9 percent <sup>pure</sup> ~~pure~~; the main impurities were: Sn < 0.0001 percent, Bi < 0.0001 percent, Pb - 0.00017, Cd < 0.0001 percent; Cu < 0.001 percent, Sb < 0.0001 percent, Zn < 0.0005 percent,

Mg < 0.0005 percent, Fe-0.0023 percent and Al < 0.0005 percent. The alloys were prepared in an arc furnace with a tungsten element on a water-cooled copper base in an argon atmosphere. Alloys were prepared in 30 g specimens and the weight of ingots was practically the same as the weight of the respective charges. We therefore assumed that the composition of alloy corresponded to the composition of the charge. In all 7 Fe-Cr, 3 Cr-Mo, 3 Cr-W, 38 Fe-Cr-Mo and 39 Fe-Cr-W alloys were prepared, the compositions of which are given in Tables 1 and 3.

Cast alloys were investigated by microstructural analysis. Using differential thermal analysis, temperatures of the beginning of melting were also determined for certain cast alloys in order to select appropriate temperatures for diffusion annealing. The alloys were subjected to the following heat treatment. Iron-chromium, chromium-molybdenum and iron-chromium-molybdenum alloys were annealed at 1400°C for 55 hours. Chromium-tungsten and iron-chromium tungsten alloys were annealed at 1450°C for 55 hours and then at 1275°C for 160 hours. All of the alloys, preliminarily annealed at 1400°C or 1450°C, were subsequently annealed at 1100°C for 270 hours. Annealing at 1275, 1400 and 1450°C was conducted in a TVV-2M furnace in an argon atmosphere, and 1100°C annealing was conducted in sealed quartz ampules, which were evacuated and filled with argon prior to sealing. After annealing in TVV-2M the alloys were cooled together with the furnace and after 1100°C annealing they were quenched in water by breaking of the ampules.

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Specimens for microstructural analysis and powders for x-ray diffraction analysis were prepared from specimens annealed at 1450, 1400,

1275 and 1100°C. Powders were prepared by filing or crushing in a mortar depending on the mechanical properties of the alloy. Specimens for microsections and powders were tempered from the temperature of annealing (1450, 1400, 1275 and 1100°C) in thin walled molybdenum cups with covers. Castor oil was used as the quenching medium. X-ray diffraction patterns were obtained on rotating powder specimens in a cylindrical camera, 57.3 mm in diameter with unfiltered radiation of the chromium anode. Cross sections for microanalysis were produced by mechanical methods using water suspension of chromium oxide on the polishing cloth. Polished cross sections were etched by the electrolytic method in an electrolyte consisting of 100 ml of acetic acid, 5 ml of perchloric acid at 25-30 v potential and current density of the order of 0.2-0.5 A/cm<sup>2</sup>. The microhardness was measured using a PMT-3 instrument with a 50 g load.

Differential thermal analyses of annealed alloys, containing up to 60 percent chromium, were conducted. Original devices, used for the preparation, annealing and thermal analysis of alloys were described in detail in reference 10. The hardness at elevated temperatures was determined in a vacuum using a VIM-1M instrument at 20, 600, 800 and 1000°C by impressing a diamond pyramid into the specimen under 1 kg load (duration of the application of pressure was 20 sec). The comparative resistance to scale formation was determined for the gain of weight (in some cases from the weight loss) after annealing at 1100°C for 8 hours in a quiescent air atmosphere.

TABLE 1. COMPOSITION OF CR-FE-MO ALLOYS.

Alloy Number	Cr wt %	Fe wt %	Mo wt %	Alloy No.	Cr wt %	Fe wt %	Mo wt %	Alloy No.	Cr wt %	Fe wt %	Mo wt %	Alloy No.	Cr wt %	Fe wt %	Mo wt %
1	90	10	—	13	60	10	30	25	40	55	5	37	30	50	20
2	80	20	—	14	55	40	5	26	40	50	10	38	30	45	25
3	70	30	—	15	55	35	10	27	40	35	15	39	30	40	30
4	60	40	—	16	50	45	5	28	40	40	20	40	25	55	20
5	55	45	—	17	50	40	10	29	40	35	25	41	25	50	25
6	50	50	—	18	50	35	15	30	40	30	30	42	25	45	30
7	45	55	—	19	50	30	20	31	35	55	10	43	20	55	25
8	80	10	10	20	50	20	30	32	35	50	15	44	20	50	30
9	70	20	10	21	45	50	5	33	35	45	20	45	15	55	30
10	70	10	20	22	45	45	10	34	35	40	25	46	90	—	10
11	60	30	10	23	45	40	15	35	35	35	30	47	80	—	20
12	60	20	20	24	45	35	20	36	30	55	15	48	70	—	30

The cross section of the Cr-Fe-Mo ternary phase diagram at 1100°C, constructed from the results of phase analyses of alloys, is shown in figure 2. The difference between  $\sigma$  and  $\chi$  phases was determined by the x-ray diffraction method. The solubility of molybdenum in the  $\alpha$ -phase is 6-7 percent when the concentration of chromium is 45-65 percent. This is in good agreement

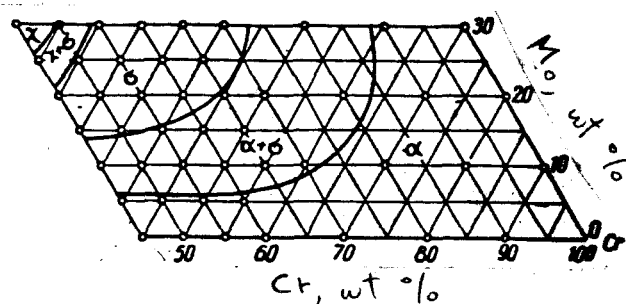


Figure 2. 1100°C isothermal cross section for the Cr-Fe-Mo phase diagram.



with the results of other authors.  $\chi$ -phase is just as brittle as  $\sigma$ -phase and therefore a small amount of either of these two phases in alloys causes them to become quite brittle. Eight polythermal cross sections of the Cr-Fe-Mo ternary phase diagrams are shown in figure 3. They were constructed from the data of this work (solid points), as well as from the results of the investigations of other authors (open circles with numbers next to them which designate the references in the <sup>bibliography. Within the</sup> bounds of the investigated concentration, both the  $\chi$ -phase and the  $\sigma$ -phase are formed not from the melt, as is assumed in (ref. 9), but from the solid  $\alpha$ -phase. As the concentration of molybdenum increases, the temperature of formation of  $\sigma$ -phase is increased significantly, but it still does not reach the solidus surface. /112

While in binary Fe-Cr alloys  $\sigma$ -phase is formed only below 900°C and <sup>over a</sup> ~~upon~~ prolonged waiting, <sup>period,</sup> which sometimes amounts to thousands of hours, upon the addition of 20-30 percent molybdenum,  $\sigma$ -phase is formed already at 1300-1400°C. Here in order to produce it, prolonged annealing is not required. It is formed in the process of cooling of the alloy. Moreover at the same concentration of molybdenum <sup>it</sup> is not possible to supercool  $\alpha$ -phase to room temperature even by quenching small specimens in oil. Thus, molybdenum stabilizes the  $\sigma$ -phase. For this reason the interpretation of thermograms for high molybdenum alloys enables one to determine reliably not only the temperature of the beginning and of the end of melting and crystallization of alloys, but also the temperature of decomposition and formation of the  $\sigma$ -phase under conditions of continuous heating or cooling of alloys. In alloys containing less than 12-17 percent molybdenum and naturally in Fe-Cr binary alloys  $\alpha \rightleftharpoons \sigma$  transformations do not take place under continuous heating and cooling conditions and thus are not apparent on the thermograms.

TABLE 2. HARDNESS AND STABILITY TO OXIDATION OF  
Cr-Fe-Mo ALLOYS AT ELEVATED TEMPERATURES.

Alloy No.	Oxidation speed		Hardness (kg/mm <sup>2</sup> ) at temp's.			
	wt gain mg/cm <sup>2</sup> ·hr	wt loss mg/cm <sup>2</sup> ·hr	20° C	600° C	800° C	1000° C
3	0,235	—	—	—	—	—
5	0,195	—	515	339	168,2	57,2
7	0,0003	—	378	313	140,2	42,1
11	1,590	—	742	613	413	205
14	0,431	—	742	439	330	171,4
15	22,36	99,2	551	482	330	135,4
16	0,389	—	498	439	305	128,8
17	21,10	93,2	571	453	401	168,2
18	9,75	57,7	742	742	515	290
19	1,352	—	916	742	636	439
20	—	0,0002	840	742	636	413
21	1,56	—	453	339	205	5,92
22	17,73	34,75	636	482	339	168,2
23	18,32	—	—	—	—	—
24	0,065	—	—	—	—	—
25	0,37	—	—	—	—	—
26	22,3	123,5	840	613	571	742
27	20,9	—	—	—	—	—
28	22,0	4,431	—	—	—	—
29	11,25	106,9	—	—	—	—
30	3,80	159,0	1159	958	840	613

NOTE: Commas in all tables represent decimal points.

Consideration of the polythermal slices (see fig. 3) shows a good agreement between the results obtained by different authors for temperatures above 800-900°C. The observed discrepancies below these temperatures can apparently be explained by the insufficient annealing, i.e., the alloys are not brought to the same equilibrium state.

The results of the determination of the hardness and oxidation stability of Cr-Fe-Mo alloys at elevated temperatures are given in Table 2. The hardness of alloys containing a significant amount of  $\sigma$ -phase was not determined

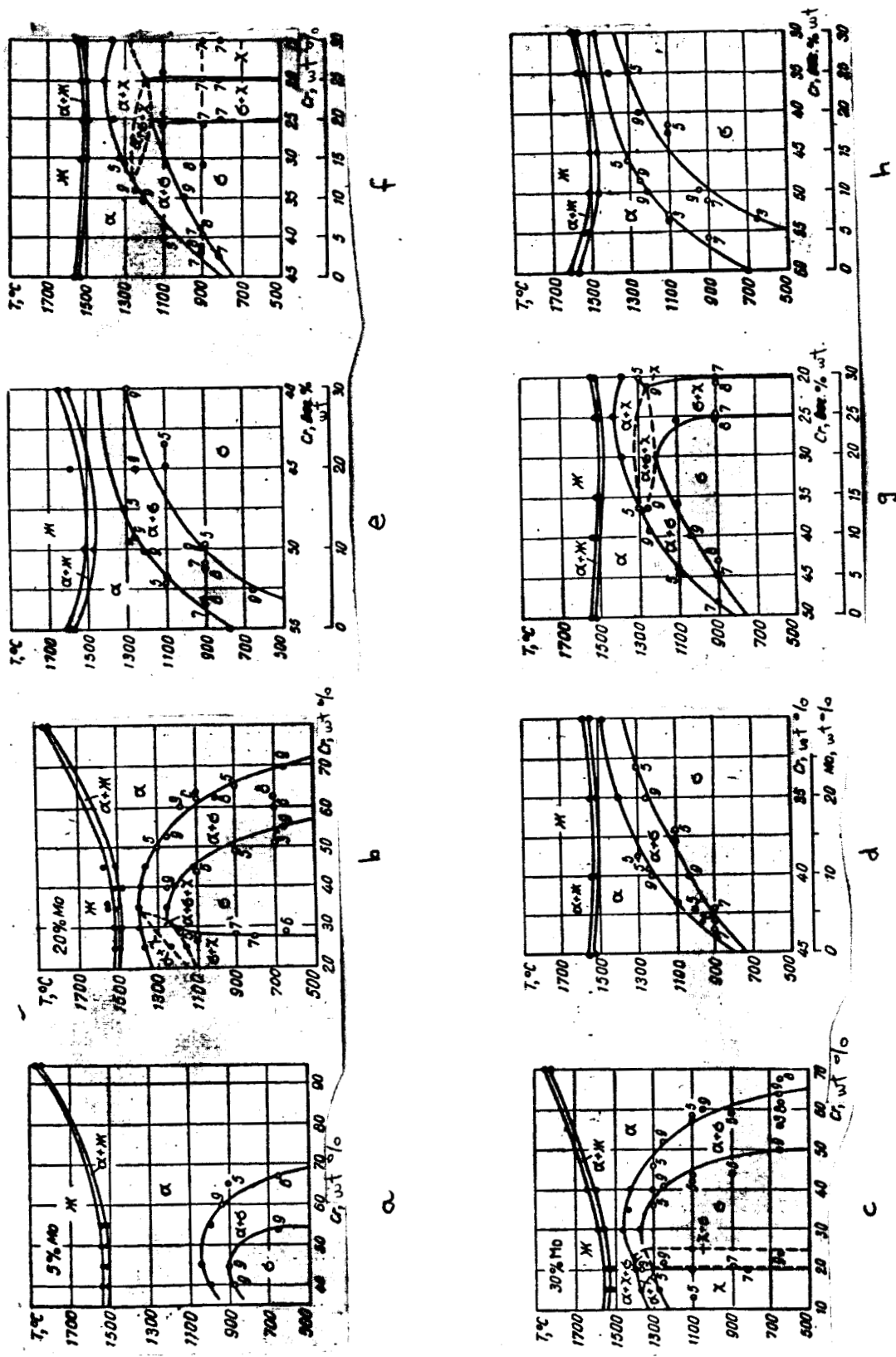


Figure 3. Polythermal cross sections of the Cr-Fe-Mo phase diagram.

Ж = liquid

due to complexity of the production of specimens from the hard and brittle material.

Specimens for hardness tests were produced from ingots subjected to diffusion annealing at  $1100^{\circ}\text{C}$  for 270 hours. At elevated temperatures the hardness of all alloys significantly decreases. The lowest hardness was displayed by the binary Fe-Cr alloys containing 45-55 percent Cr. During the formation of  $\sigma$ -phase the hardness of alloys sharply increases. Here the lowering of the hardness of alloys with increase of the temperature is much smaller than in alloys which do not contain the  $\sigma$ -phase. /115

In alloys with constant concentration of Fe 45-50 percent the increase of the concentration of molybdenum has practically no effect on the hardness within the limits of  $\alpha$ -solid solution both at room temperature and at elevated temperatures.

The rate of oxidation of specimens was measured either as the gain of weight due to gain of oxygen (per unit area and per unit time), which characterizes sufficiently well the stability to oxidation of those alloys which do not form volatile oxides, or as the weight loss of the metal specimen, which is used for those alloys which form volatile oxides. Since oxides of molybdenum are volatile, the rate of oxidation on the basis of the gain of weight was evaluated only for those alloys in which the concentration of molybdenum did not exceed 10 percent. In the case of high concentration of molybdenum the extent of oxidation of alloys was evaluated from the loss of weight of metal specimens (see Table 2).

Because of short duration of the cited tests of alloys for oxidation stability the results should be considered only as comparative oxidation

stability in the initial stages of the process. Despite this the comparison of the test results (see Table 2) enables one to conclude that concentrations of molybdenum up to 5 percent, i.e., within the bounds of  $\alpha$ -solid solution, /116 has practically no effect on the oxidation stability of alloys.

In the case when  $\sigma$ -phase is present oxidation becomes significantly worse.

The phase diagram of the investigated part of the Cr-Fe-W system was constructed on the basis of differential thermal analysis of alloys, annealed at 1450°C.

The thermograms of all the investigated alloys with the exception of alloy No. 2 (30 percent Cr, 30 percent W) display heat effects of melting and crystallization of the single phase solid solution. In different alloys these effects differ only in the temperatures of the beginning and the end of the transformation. This indicates that in the whole investigated concentration interval (with the exception of the corner in the region of No. 2 alloy) the solidus surface bounds the region of the single-phase  $\alpha$ -solid solution. The thermogram for No. 2 alloy shows a double thermal effect of melting and crystallization. This should be interpreted as the existence of two phase regions between solidus and liquidus, in this case  $\alpha + \zeta + \text{liquid}$  and  $\alpha + \text{liquid}$  (see below).

Figure 4 shows the solidus surface of the investigated part of the Cr-Fe-W ternary system in the form of a projection onto the plane of the concentration triangle with isotherms spaced at 50°C intervals and  $\alpha$  line for monovarying equilibria (designated by the line ---). This is a maximum solubility line for tungsten and iron in  $\alpha$ -solid solution.

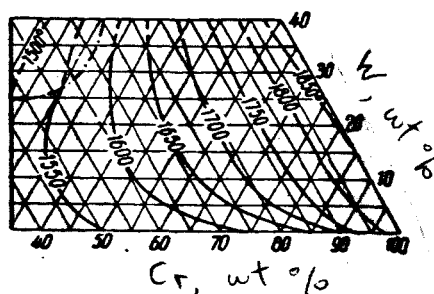
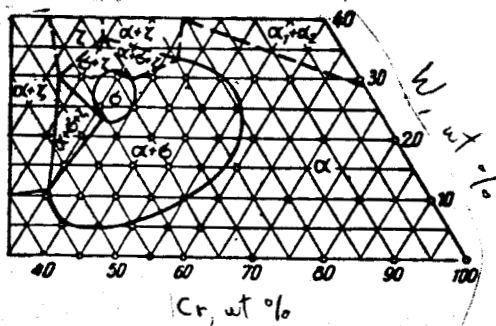
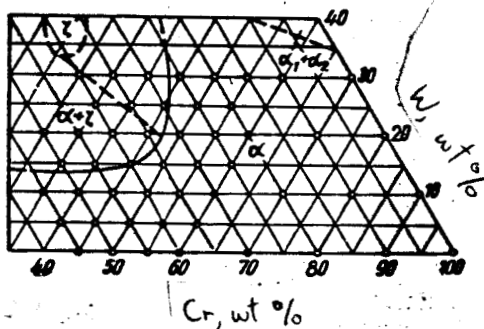


Figure 4. Solidus surface of the Cr-Fe-W system in the form of a projection onto the plane of the concentration triangle.

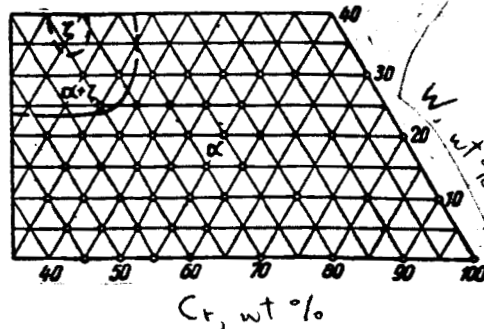
The phase equilibrium diagram of the ternary system in the solid state was constructed by the investigation of isothermal cross sections. Isothermal cross sections were constructed at 1100, 1275 and 1450°C (fig. 5). In order to construct phase boundaries on these cross sections, quenching and X-ray diffraction analysis as well as quenching and microstructural analysis were used. The boundary between the single phase  $\alpha$ -region and the two phase  $\alpha + \sigma$  region on 1275°C and 1450°C slices was constructed primarily on the basis of microstructural analysis data. The boundary between  $\alpha$  and  $\alpha + \sigma$  regions was constructed on the basis of X-ray structural analysis data. For this purpose, from X-ray diffraction patterns of alloys quenched after 1100°C annealing, the crystal lattice parameter (body-centered cubic) of  $\alpha$ -solid solution was determined (from the reflection from the (211) plane). Following this, reflection points which correspond to the passage through the phase boundary were determined on the lattice parameter of the  $\alpha$ -solid solution plot as a function of the composition of the alloy. Some of the graphs of the lattice parameter of the  $\alpha$ -phase as a function of the composition of the alloy are shown in figures 6a and 6b. The other phase region boundaries



1100°C



1275°C



1450°C

Figure 5. Isothermal cross sections of the Cr-Fe-W phase diagram at different temperatures.

are constructed approximately on the basis of microstructural and X-ray phase analyses. It should be noted that for alloys containing 20-30 percent tungsten and 30-45 percent iron the rate of cooling during tempering of powders /117

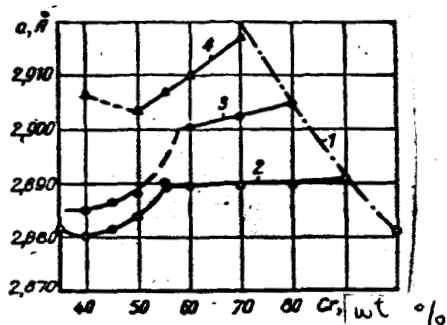


Figure 6a. Lattice parameter of the  $\alpha$ -solid solution as a function of the composition of Cr-W alloy after annealing at  $1100^{\circ}\text{C}$ . 1- Cr-W binary alloys; 2- cross section at 10 percent W; 3- cross section at 20 percent W; 4- cross section at 30 percent W.

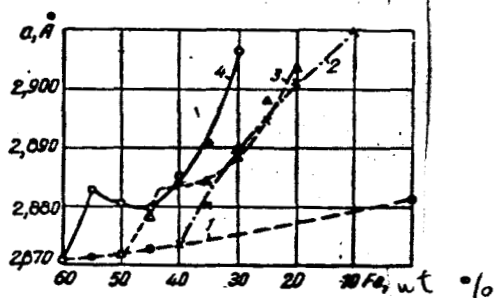


Figure 6b. Lattice parameter of the  $\alpha$ -solid solution as a function of the composition of Cr-Fe alloy after annealing at  $1100^{\circ}\text{C}$ . 1- Cr-Fe binary alloys; 2- 60 percent Cr cross section; 3- 50 percent Cr cross section; 4- 40 percent Cr cross section.



in molybdenum cups from 1275-1450°C was apparently insufficient for quenching the high temperature state. As result, for certain alloys the data of ~~X~~-ray structural and microstructural phase analysis are in disagreement. In these cases the data of microstructural analyses is considered more reliable since during tempering the rate of cooling of specimens designated for microanalysis was higher. A number of alloys, consisting of two phases according to ~~X~~-ray data, displayed only single phase according to microstructural analysis. It should also be noted that in alloys Nos. 2, 3, and 4 during tempering of even compact specimens from 1450-1275°C, partial decomposition was observed. This is easily detected during microanalysis. The field of  $\alpha$ -solid solution is filled with fine segregations of the  $\sigma$ -phase. It is possible that during quenching in water the decomposition process could be prevented. After tempering from 1450°C all the alloys with the exception of Nos. 2, 3 and 4 had single phase ( $\alpha$ -solid solution) and had a typical polyhedral /118 microstructure of the large-grain solid solution. In the 1275°C cross section the two phase ( $\alpha + \zeta$ ) alloy region broadens. However, in the case of 1450°C as well as 1275°C the  $\sigma$ -phase is present only in alloy Nos. 2, 3 and 4 in the form of fine segregations, which indicates its formation during insufficiently rapid cooling.

The decomposition of  $\alpha$ -solid solutions into two solid solutions, which was discovered in the binary chromium-tungsten alloys (ref. 1) was not investigated by us with any special attention, and only x-ray analysis of the alloy No. 37 (30 percent W), annealed at 1100°C, gives a basis for the assumption that at this temperature it falls into the two-phase  $\alpha_1 + \alpha_2$  region, but close to its boundaries, and therefore it was not possible to obtain a clear-cut splitting of ~~X~~-ray diffraction lines.

Thus, by examining isothermal slices of phase diagrams one can conclude that phase regions present on the cross section at 1100°C along with  $\sigma$ -phase ( $\sigma$ ,  $\sigma + \zeta$ ,  $\alpha + \sigma$ ,  $\alpha + \sigma + \zeta$ ) disappear at 1275°C and the 1450°C cross section generally does not differ from the 1275°C cross section. Therefore, the  $\sigma$ -phase region is dome-shaped and it is wedged out with increase of temperature. Two  $\alpha + \sigma + \zeta$  three-phase regions which exist in the 1100°C cross section (see fig. 5a) must merge at the apex of the  $\sigma$ -phase dome. According to the phase rule they can merge only by degenerating into a straight line resting with its ends on single phase regions  $\alpha$  and  $\zeta$  and passing as a tangent to the apex of the  $\sigma$ -phase dome. This straight line corresponds to the invariant three phase equilibrium  $\alpha + \zeta \rightleftharpoons \sigma$  (an approximate position of this straight line is shown in figure 5b by a broken line). It is a transition from two degenerate tie line triangles of the  $\alpha + \sigma + \zeta$  to the  $\alpha + \zeta$  tie /119 line. It would appear at first glance that in the ternary system  $\alpha + \zeta \rightleftharpoons \sigma$  equilibrium <sup>u</sup> cannot be nonvariant. However, if one remembers the case in binary systems when a two phase equilibrium is nonvariant, such as  $\alpha \rightleftharpoons \sigma$  during the formation of  $\sigma$ -phase, liquid  $\rightleftharpoons \alpha$  at minimum and maximum on solidus and liquidus curves, then by analogy one must admit that the existence of a nonvariant three-phase equilibrium in a ternary system is possible. It turned out to be difficult to determine the temperature position of the  $\alpha + \zeta \rightleftharpoons \sigma$  equilibrium line since in the solid state the transitions through phase boundaries in the majority of cases are not detected by the differential thermal analysis, and in alloys Nos. 2, 3, 4 and 5 where thermal effects associated with decomposition and formation of the  $\sigma$ -phase (during heating and cooling) do occur, the temperature position of these effects

depends greatly on the rate of heating. Thus, in changing the rate of heating from 20 to 50 - 60 deg/min the temperature at which the thermal effect is noticed in alloy No. 5 increases from 1250 to 1350°C.

We attempted to determine the position of the  $\alpha + \zeta \rightleftharpoons \sigma$  equilibrium line during the construction of polythermal cross sections of the phase diagram. The polythermal cross sections of the diagram, parallel to the chromium-iron side (fig 7) and parallel to the iron-tungsten side (fig. 8) we constructed from the available isothermal cross sections. Solidus and liquidus were plotted on the basis of the data of differential thermal analysis. On the basis of these cross sections it was possible to obtain approximately the position of this equilibrium line. It apparently lies at 1250-1275°C. Investigation of hardness and scale resistance of the alloys at elevated temperatures was conducted with specimens annealed at 1450°C and then at 1100°C. The hardness data at 20, 600, 800 and 1000°C as well as on the resistance to scale formation at 1100°C based on the gain of weight are given in Table 3. It turned out that tungsten has little effect on the scale formation of chromium-iron alloys. Ternary alloys containing iron in excess of 15 percent and tungsten up to 30 percent are oxidized to a lesser extent than pure chromium. A slightly higher oxidizability was observed for alloys lying in the  $\alpha + \sigma$  two-phase region as compared with the single-phase alloy. The greatest oxidizability was observed for the binary chromium-tungsten alloys, but even here it was of the same order as the oxidizability of pure chromium under the same conditions. Thus, from the standpoint of resistance to scale formation tungsten is not an undesirable additive to iron-chromium alloys. If one compares the effect of tungsten and molybdenum on the resistance to scale formation of alloys of an analogous composition, the comparison is not in favor of

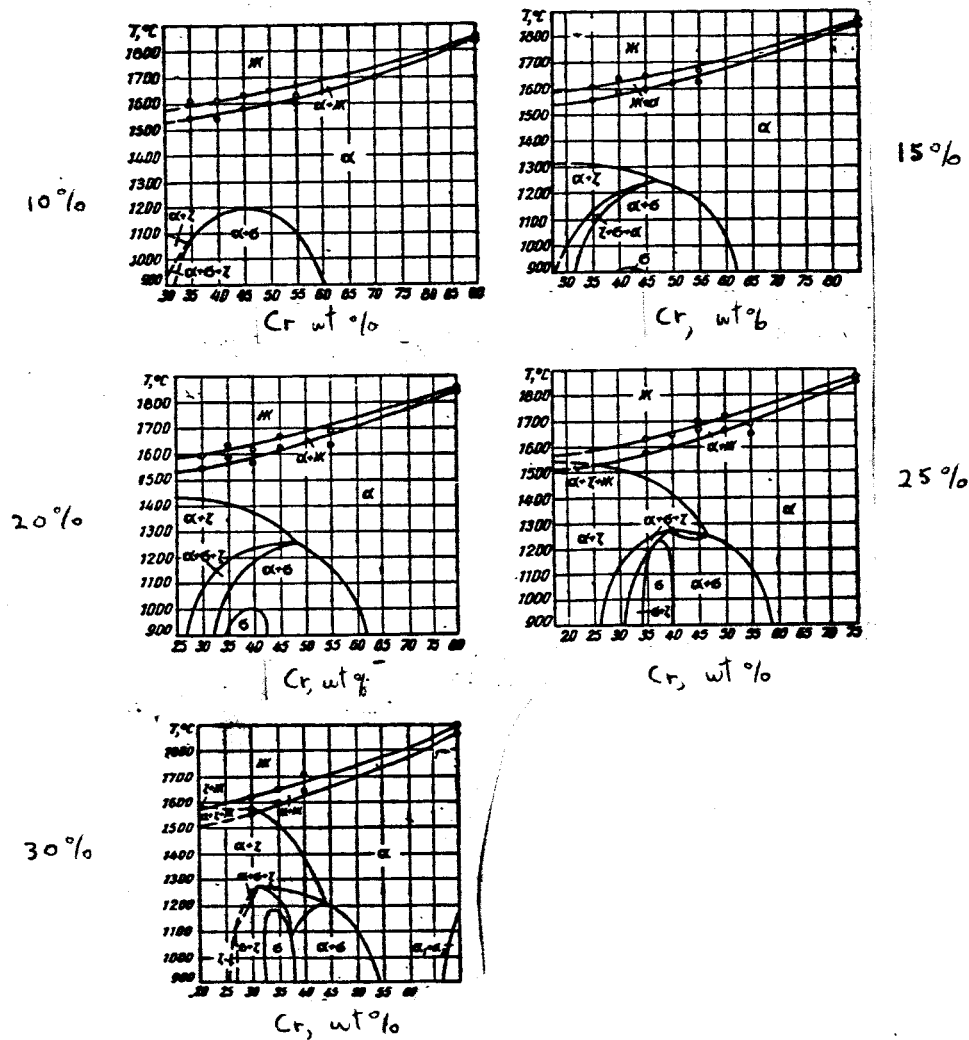


Figure 7. Polythermal cross sections of the Cr-Fe-W phase diagram with constant amount of tungsten.

molybdenum. The worst of the Cr-Fe-W alloys become coated with only a light film of oxide, while Cr-Fe-Mo alloys of <sup>analogous</sup> ~~the same~~ composition oxidize almost completely under the same conditions.

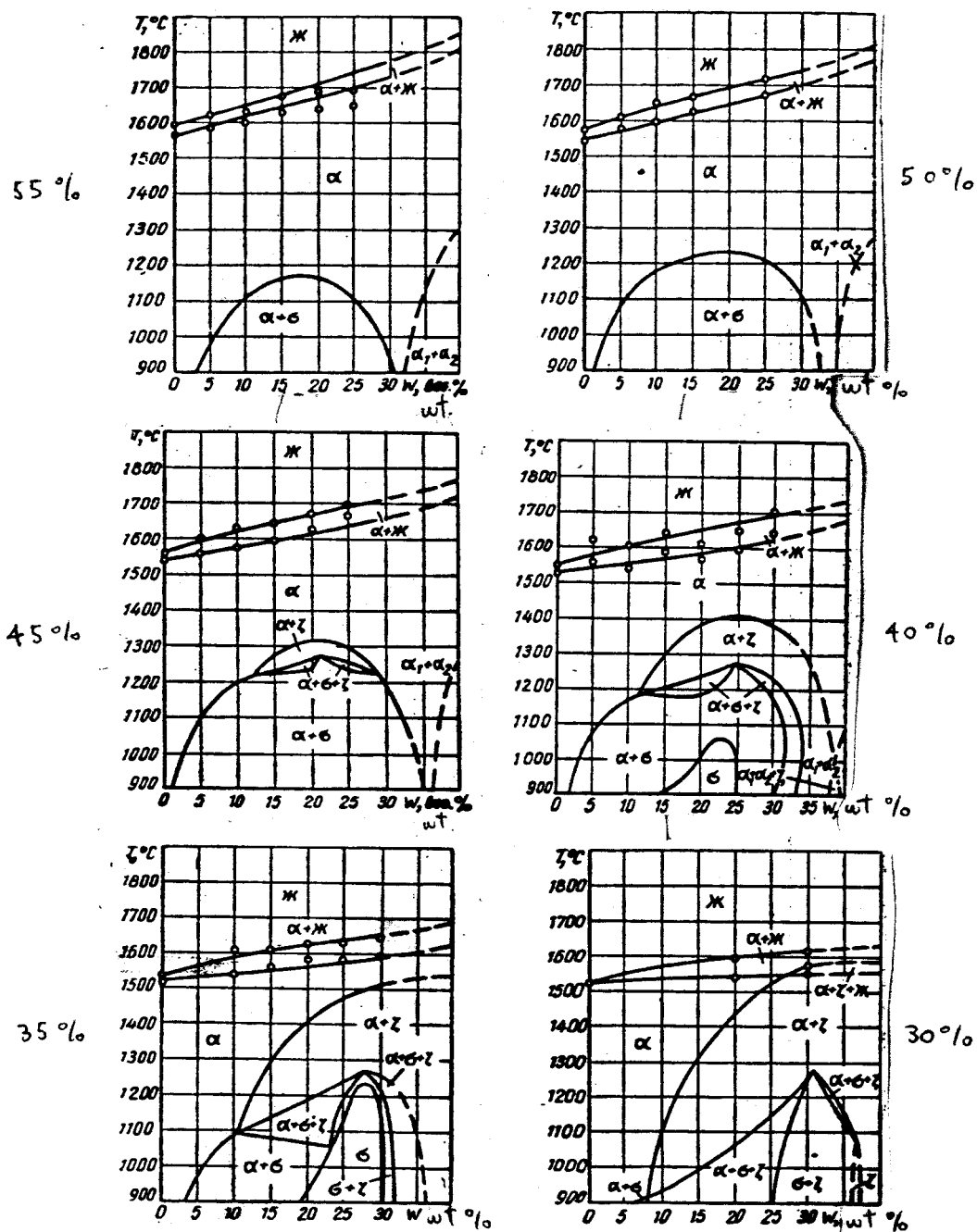


Figure 8. Polythermal cross section of the Cr-Fe-W phase diagram with constant amount of chromium.

TABLE 3. COMPOSITION, CRYSTAL LATTICE PARAMETERS OF  $\alpha$ -PHASE HARDNESS AT ELEVATED TEMPERATURES, AND OXIDATION STABILITY OF Cr-Fe-W ALLOYS.

Alloy No.	content, wt %			lattice parameters 1100°C, Å	hardness kg/mm <sup>2</sup>				sintering stability by wt gain after 1100°C annealing mg/cm <sup>2</sup> .hr
	Cr	Fe	W		20°C	600°C	800°C	1000°C	
1	30	50	20	—	—	—	—	—	—
2	30	40	30	—	—	—	—	—	—
3	35	35	30	—	—	—	—	—	—
4	35	40	25	—	—	—	—	—	—
5	35	45	20	—	—	—	—	—	—
6	35	50	15	2.8779	—	—	—	—	—
7	35	55	10	2.8814	813	421	276	186	0.5200
8	40	30	30	2.9065	876	645	589	351	0.7900
9	40	35	25	2.8906	1288	1033	920	642	0.2170
10	40	40	20	2.8850	1246	1048	813	707	0.2740
11	40	45	15	2.8796	1048	894	847	514	0.2140
12	40	50	10	2.8802	1033	752	634	363	0.4230
13	40	55	5	2.8826	—	—	—	—	—
14	45	25	30	—	—	—	—	—	—
15	45	30	25	2.8951	—	—	—	—	—
16	45	35	20	2.8865	598	520	368	182	—
17	45	40	15	2.8814	1340	949	798	507	0.6350
18	45	45	10	2.8814	—	—	—	—	—
19	45	50	5	2.8779	—	—	—	—	—
20	50	20	30	2.9032	882	599	473	387	0.4500
21	50	25	25	2.8978	724	508	464	256	0.4270
22	50	30	20	2.8882	—	—	—	—	—
23	50	35	15	2.8838	715	446	224	90	0.4370
24	50	40	10	2.8838	429	339	216	106	0.0955
25	50	45	5	2.8779	—	—	—	—	—
26	55	15	30	2.9071	724	503	437	348	0.5050
27	55	20	25	2.9032	—	—	—	—	—
28	55	25	20	2.8900	525	417	245	180	0.2700
29	55	30	15	2.8882	—	—	—	—	—
30	55	35	10	2.8894	—	—	—	—	—
31	55	40	5	2.8802	—	—	—	—	—
32	60	10	30	2.9101	—	—	—	—	—
33	60	20	20	2.9011	678	529	378	330	0.1480
34	60	25	15	2.8951	—	—	—	—	—
35	60	30	10	2.8894	498	354	266	139	0.2180
36	60	35	5	2.8802	—	—	—	—	—
37	70	0	30	2.9171	634	530	380	330	1.0360
38	70	10	20	2.9026	—	—	—	—	—
39	70	20	10	2.8900	542	419	344	187	0.3400
40	80	0	20	2.9054	421	287	254	206	1.1200
41	80	10	10	2.8900	—	—	—	—	—
42	90	0	10	2.8912	370	180	170	122	1.0100
50	100	0	0	2.8814	151	109	104	67	1.2900

The addition of tungsten in general increases the hardness of iron-chromium alloys at room temperature as well as at elevated temperatures. This effect is particularly pronounced in alloys which lie in the  $\alpha + \sigma$  two-phase region. For these alloys in the presence of a significant amount of  $\sigma$ -phase, hardness reaches 1200-1300 kg/mm<sup>2</sup>. These alloys are brittle but they can be brought into a plastic state by tempering from 1400-1450°C. It should be noted that the alloys which lie in the proximity of  $\alpha$  and  $\alpha + \sigma$  phase /120 boundaries and contain a large amount of tungsten (for example No. 20) are not brittle and at the same time their hardness is sufficiently high.

#### CONCLUSIONS

In the Cr-Fe-Mo system:

- 1) Molybdenum stabilizes the  $\sigma$ -phase which is manifested by the increase of the temperature and the rate of its formation from  $\alpha$ -phase and by broadening of the concentration interval of its stability.
- 2) Molybdenum lowers slightly the melting point of alloys. Only upon a significant increase of the concentration of molybdenum the melting point of alloys increases.
- 3) In alloys containing 45-60 percent Cr, the single-phase  $\alpha$ -region extends only to 6-7 percent molybdenum at 1000-1100°C. At high concentration of molybdenum these alloys easily form the brittle  $\sigma$ -phase.
- 4) At 45-55 percent chromium, the increase of the concentration of molybdenum to 6-7 percent at elevated temperatures has practically no effect on the hardness of alloys within the boundaries of the homogeneous  $\alpha$ -solid solution.
- 5) The hardness of alloys at elevated temperatures is significantly increased when the  $\sigma$ -phase is formed in them. The relatively high hardness of

the two-phase ( $\alpha + \sigma$ ) alloys is retained at high temperatures even when the amount of  $\sigma$ -phase is relatively small.

6)  $\sigma$ -phase is extremely unstable at  $1100^{\circ}\text{C}$  with respect to air oxidation. The oxidation stability of the ternary alloys is inversely proportional to the concentration of  $\sigma$ -phase in them.

7) Within the boundaries of the homogeneous  $\alpha$ -solution when the concentration of chromium ranges from 45 to 55 percent, the increase of the concentration of molybdenum (up to 6 percent) has practically no effect on the oxidation stability of alloys.

In the Cr-Fe-W system:

1) The single-phase  $\sigma$ -region in the ternary system extends to approximately 32 percent of tungsten and a dome is formed with the base extended towards the chromium-iron binary system. It is edged out at approximately  $1275^{\circ}\text{C}$ .

2) The disappearance of  $\sigma$ -phase in Cr-Fe-W alloys above  $1275^{\circ}\text{C}$  is apparently associated with the nonvariant  $\alpha + \zeta \rightleftharpoons \sigma$  three phase equilibrium, the existence of which is based on the considerations <sup>of phase composition</sup> changes in the isothermal cross sections at  $1100$ ,  $1275$  and  $1450^{\circ}\text{C}$ .

3) At high temperature ( $1450^{\circ}\text{C}$ ) the single-phase region of  $\alpha$ -solid solution with body centered cubic lattice undergoes significant expansion. It was found that all of the investigated alloys with the exception of No. 2 (40 percent iron and 30 percent tungsten) convert to the single phase at relatively high temperatures.

4) It was shown that the single-phase state can be easily captured by quenching. In all of the alloys, with the exception of Nos. 2, 3 and 4,



quenching from 1450°C in castor oil produces a single phase structure and alloys become relatively plastic.

5) The addition of tungsten results in a slight increase <sup>in</sup> of the melting point of chromium-iron alloys (30 percent of tungsten increases the temperature of solidus in the cross section containing 40 percent chromium by 100°C and on the 50 percent Cr cross section by 150°C).

6) The addition of tungsten increases the hardness of alloys at room temperature as well as at elevated temperatures. This increase is especially pronounced in the  $\alpha + \sigma$  two-phase region.

7) Tungsten has no adverse effect on the resistance of chromium-iron alloys to scale formation. The resistance to scale formation of all of the investigated alloys was not less than the resistance of pure chromium.

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